

Fundamental data on the desorption of pure interstellar ices

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ABSTRACT

The desorption of molecular ices from grain surfaces is important in a number of astrophysical environments including dense molecular clouds, cometary nuclei and the surfaces and atmospheres of some planets. With this in mind, we have performed a detailed investigation of the desorption of pure water, pure methanol and pure ammonia ices from a model dust-grain surface. We have used these results to determine the desorption energy, order of desorption and the pre-exponential factor for the desorption of these molecular ices from our model surface. We find good agreement between our desorption energies and those determined previously; however, our values for the desorption orders, and hence also the pre-exponential factors, are different to those reported previously. The kinetic parameters derived from our data have been used to model desorption on time-scales relevant to astrophysical processes and to calculate molecular residence times, given in terms of population half-life as a function of temperature. These results show the importance of laboratory data for the understanding of astronomical situations whereby icy mantles are warmed by nearby stars and by other dynamical events.

Key words: molecular data – molecular processes – methods: laboratory – ISM: molecules.

1 INTRODUCTION

Recent work (e.g. Collings et al. 2004; Viti et al. 2004) has shown the importance of using experimentally determined kinetic parameters to describe the desorption of icy mantles from grain surfaces. Desorption processes have been found to be particularly important in hot-core regions (Williams 1998; Viti et al. 2004). Hot cores are small, dense, relatively warm, optically thick and transient objects detected in the vicinity of newly formed massive stars. Hot cores exhibit a range of molecular species due to the evaporation of processed ice, formed during the star formation process. As well as giving an understanding of the chemistry of hot cores (Viti et al. 2004; Brown et al. 2006), data of this type can also be used to determine molecular residence times of ices on grain surfaces as a function of temperature. These residence times are useful as they provide a measure of the ice stability with respect to sublimation. Understanding ice sublimation is important in a number of astrophysical environments including dense molecular clouds, cometary nuclei and the surfaces and atmospheres of planets. With this in mind, we have undertaken a detailed study of the adsorption and desorption of pure water (Bolina, Wolff & Brown 2005a), pure methanol (Bolina, Wolff & Brown 2005b) and pure ammonia (Bolina & Brown 2005) ices from a model dust-grain surface and the results of these experiments, and resulting astrophysical simulations, are described here.

Water (H_2O) is the most abundant species in molecular ices in dense interstellar regions (Whittet 1993, 2003; Ehrenfreund &

Schutte 2000) and hence it plays a significant role in the chemistry of the interstellar medium (ISM). A clear understanding of the adsorption and desorption of H_2O is therefore crucial in understanding gas–grain interactions and, in turn, the chemistry of the ISM. H_2O exists in a number of different forms on grain surfaces, including high- and low-density amorphous ice and crystalline ice (Jenniskens & Blake 1994, 1996; Fraser et al. 2001), and the physical properties of the ice are dictated by its structure. Furthermore, it has been shown that for mixed ices that contain H_2O , the desorption of all species in the ice is controlled by the behaviour of the H_2O (Collings et al. 2004).

Methanol (CH_3OH) is also found in the ISM, frozen out on the surface of dust grains (Gibb et al. 2004) and is one of the more commonly detected species in molecular ices. It has been found to have an abundance of between 5 and 50 per cent of that of H_2O (Sandford & Allamandola 1993; Pontoppidan et al. 2003; Pontoppidan, van Dishoeck & Dartois 2004). CH_3OH influences both the chemical and physical properties of interstellar ices and hence affects their sublimation. As for H_2O , it is therefore important to have accurate kinetic parameters that describe the desorption of CH_3OH from grain surfaces.

Ammonia (NH_3) is also an important molecule in the ISM. Dust grains can provide an opportunity for freeze-out of NH_3 at low temperatures and are also implicated in its formation by the surface catalysed hydrogenation of N atoms. The importance of NH_3 in the ISM has been demonstrated by the observation of NH_3 in interstellar ices (Whittet 1993), where it has been found to have an abundance of around 5–30 per cent relative to water ice (Whittet et al. 1996; Lacy et al. 1998; Chiar et al. 2000; Dartois & d’Hendecourt 2001; Gibb,

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Whittet & Chiar 2001). NH_3 is also an important carrier of nitrogen in the ISM and is involved in many reactions involving nitrogen chemistry (Tielens & Hagen 1982; Nejad, Williams & Charnley 1990). Hence a complete understanding of the interaction of NH_3 with dust-grain surfaces, and its sublimation from those surfaces, is required to accurately model the chemistry of the ISM.

Previous studies of the desorption of H_2O ice from a CsI surface determined surface binding energies from spectroscopic data (Sandford & Allamandola 1988). The studies found that the binding energy of H_2O on H_2O ice was 4815 ± 15 and 5070 ± 50 K for unannealed and annealed ice samples, respectively. These studies assumed that the H_2O desorption obeyed first-order kinetics. A more recent study (Fraser et al. 2001) used a direct experimental method to show that H_2O ice desorption from a Au surface obeys zero-order kinetics. This study found that the H_2O had a surface binding energy of 5773 ± 60 K and a pre-exponential factor of $10^{34 \pm 2}$ molecules $\text{m}^{-2} \text{s}^{-1}$. The discrepancy between these previous studies has important implications for our understanding of the desorption of H_2O ice from grain surfaces and hence further studies are essential.

There has been only one previous reported investigation of the binding energies of CH_3OH and NH_3 in model interstellar ices (Sandford & Allamandola 1993). Spectroscopic data were used to give a binding energy for CH_3OH on CH_3OH ice of 4235 ± 15 K and for NH_3 on NH_3 ice of 3075 ± 25 K. Both CH_3OH and NH_3 were assumed to obey first-order desorption kinetics with pre-exponential factors of 2.2×10^{12} and $3.45 \times 10^{12} \text{ s}^{-1}$, respectively (Sandford & Allamandola 1993).

This paper describes the results of a detailed study of the desorption of pure H_2O (Bolina et al. 2005a), pure CH_3OH (Bolina et al. 2005b) and pure NH_3 (Bolina & Brown 2005) ices from a model dust-grain surface. The detailed kinetics of the desorption of these species have been obtained directly from experimental data and have been used to model desorption on time-scales relevant to the ISM. Molecular residence times, given in terms of population half-life as a function of temperature, have also been determined. The surface used in the experiments to model a dust grain is highly oriented pyrolytic graphite (HOPG). HOPG, and other carbon-based surfaces, can be considered suitable analogues of dust grains and have previously been used in investigations of H_2 formation on dust-grain surfaces (Katz et al. 1999; Pirronello et al. 1999; Perry et al. 2002; Perry & Price 2003). This study is the first to perform simulations using kinetic parameters derived directly from experimental data on grain-like surfaces and comparisons with previous data allow us to determine whether the nature of the surface is important in determining desorption from dust grains. Note that the nature of the surface is likely to be more important for thin ices than for thick ices and also more important for strongly bound molecular species than for weakly bound species.

2 EXPERIMENTAL METHOD

The apparatus used for the experiments reported here has been described elsewhere (Bolina et al. 2005a,b), therefore only a brief description will be given here. Experiments were performed in an ultrahigh vacuum apparatus that has a base pressure of $\leq 2 \times 10^{-10}$ mbar. The HOPG sample was cooled to ~ 90 K and the molecular ices were deposited at this temperature. Although this temperature is higher than that observed in the ISM (where ice covered grains have a temperature of 10–20 K), the results obtained still allow an understanding of the sublimation of interstellar ices from grain surfaces to be obtained. Previous results for the desorption of molecular ices from a Au surface (Collings et al. 2004) show that H_2O , CH_3OH

and NH_3 do not desorb at temperatures below 100 K. Note that the complex desorption observed by Collings et al. (2004) is not observed here, as these experiments were all performed to investigate the desorption of pure, not mixed, molecular ices.

The desorption of each pure molecular species from the HOPG surface was monitored as a function of exposure in units of Langmuir (L_m) where $1L_m = 1 \times 10^{-6}$ mbar s. We were not able to make an accurate measurement of surface coverage in these experiments; however, we estimate that the maximum thickness of our ices, following a $300L_m$ exposure, corresponds to ~ 5 monolayers. A pure dose of each species was introduced into the chamber by the use of a high-precision leak valve. Desorption of the ices was monitored using temperature-programmed desorption (TPD). TPD spectra for CH_3OH and H_2O desorption were recorded using a heating rate of $0.50 \pm 0.01 \text{ K s}^{-1}$ and those for NH_3 desorption were recorded with a heating rate of $0.20 \pm 0.01 \text{ K s}^{-1}$. Kinetic parameters for the desorption of the pure ices were extracted from the TPD data using the methods described previously (Bolina & Brown 2005; Bolina et al. 2005a,b). The kinetic parameters thus obtained were then used to determine the desorption temperature for icy mantles from grain surfaces under astrophysical conditions and to determine the molecular residence times of the pure ices on the grain surfaces as a function of temperature.

3 RESULTS AND DISCUSSION

3.1 Experimental results

Fig. 1 shows example TPD spectra recorded for the desorption of increasing thicknesses of pure H_2O ice from an HOPG surface (Bolina et al. 2005a). As already discussed, exposure is measured in L_m . With the dosing set-up used in the experiments described here, we estimate that a dose of $100L_m$ corresponds to an ice film of $\sim 5 \times 10^{19}$ molec m^{-2} . The ices are grown at a temperature of ~ 90 K, and hence are made up of low-density amorphous ice, which has a density of 940 kg m^{-3} (Jenniskens et al. 1995). This gives an estimated ice thickness of ~ 2 nm for the $100L_m$ exposure H_2O ice film.

The TPD peaks observed in Fig. 1 are assigned to the desorption of H_2O from various different phases adsorbed on the HOPG surface. Peak A is attributed to the desorption of H_2O from the two-dimensional islands that are formed on the surface at very low exposures of H_2O ice. Peak B arises due to the desorption of multilayers of H_2O ice that grow on the surface with increasing exposure. The observation of peaks C and D can be assigned to phase changes that take place as a result of the TPD heating process. Peak C signifies the phase change of amorphous to crystalline H_2O ice and peak D is assigned to a further phase change of crystalline ice to hexagonal ice (Bolina et al. 2005a). Note that the phase transition that gives rise to peak C is believed to occur for all ice thicknesses that lead to the formation of multilayers. However, peak C can only be observed in the TPD spectrum for higher exposures of H_2O ice. This is because, at the experimental heating rate ($0.50 \pm 0.01 \text{ K s}^{-1}$), thinner ices are completely converted from the amorphous to the crystalline phase before desorption occurs (Bolina et al. 2005a). Hence, only peak B is observed in the TPD spectrum for thinner H_2O layers. Note that peak B arises due to the desorption of crystalline multilayers of H_2O ice that are formed on the HOPG surface as a result of the TPD heating process.

TPD spectra have also been recorded for the desorption of pure CH_3OH ice from an HOPG surface (fig. 4, Bolina et al. 2005b). As for H_2O desorption, several different TPD peaks are seen as a function of increasing exposure. At low exposures, the desorption

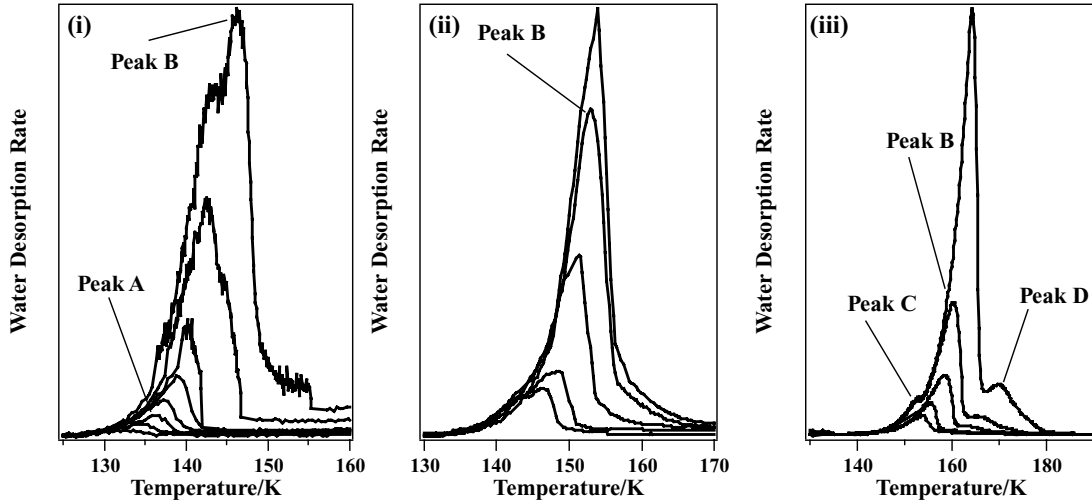


Figure 1. TPD spectra recorded following increasing exposures of H₂O on an HOPG surface initially at 90 K. Panel (i) shows spectra recorded following doses of 0.04, 0.06, 0.1, 0.2, 0.3, 0.4, 1 and 2 L_m of H₂O; panel (ii) shows spectra recorded following doses of 2, 3, 7, 10 and 15 L_m of H₂O and panel (iii) shows spectra recorded following doses of 15, 20, 50, 100 and 275 L_m of H₂O. The rate of desorption in each graph is given in arbitrary units. Adapted with permission from J. Phys. Chem. B, 2005, 109, 16836. Copyright 2005 American Chemical Society.

Table 1. Table showing the kinetic parameters previously derived for the desorption of pure H₂O, pure CH₃OH and pure NH₃ ices from an HOPG surface (Bolina et al. 2005a,b; Bolina & Brown 2005). These parameters have been used to simulate the desorption of pure molecular ices under astrophysical conditions.

| | Desorption order n | Desorption energy (K) | Pre-exponential factor ^a (molec m ⁻² s ⁻¹) |
|-------------------------------|----------------------|-----------------------|--|
| H ₂ O | 0.26 ± 0.02 | 4799 ± 96 | $1 \times 10^{27 \pm 1}$ |
| NH ₃ | 0.25 ± 0.05 | 2790 ± 144 | $8 \pm 3 \times 10^{25}$ |
| CH ₃ OH multilayer | 0.35 ± 0.21 | 4931 ± 98 | $6 \times 10^{25 \pm 3}$ |
| CH ₃ OH monolayer | 1.23 ± 0.14 | 5773 ± 95 | $9 \times 10^{9 \pm 3b}$ |

^aThe units given for the pre-exponential factors for H₂O, NH₃ and CH₃OH multilayers are those for zero-order desorption, despite the fractional desorption order obtained from the data; ^bthe units given for the pre-exponential factor for monolayer CH₃OH are those for first-order desorption (s⁻¹) despite the fractional desorption order obtained from the data.

of monolayer CH₃OH from the HOPG surface is observed. With increasing exposure, the desorption of CH₃OH multilayers is seen and at very high exposures a phase transition, that occurs as a result of the TPD heating process, leads to the observation of a high-temperature shoulder on the TPD spectra. This shoulder is observed due to the formation of crystalline CH₃OH (Bolina et al. 2005b).

The desorption of pure NH₃ ice from the HOPG surface has also been investigated using TPD (fig. 3, Bolina & Brown 2005). Two desorption features are seen in the spectra as a function of increasing exposure. An initial, low-temperature, peak observed following low doses of NH₃ on to the HOPG surface is assigned to the desorption of monolayers of NH₃. A larger, high-temperature, peak which increases in temperature with increasing NH₃ coverage is assigned to the desorption of multilayer NH₃ (Bolina & Brown 2005).

TPD spectra are described by the Polanyi–Wigner equation (de Jong & Niemantsverdriet 1990):

$$r_{\text{des}} = -\frac{d\theta}{dt} = \nu_n \theta^n \exp\left(\frac{-E_{\text{des}}}{RT}\right), \quad (1)$$

where r_{des} is the rate of desorption, ν_n is the pre-exponential factor for the desorption process of order n , θ is the surface coverage, E_{des} is the desorption energy, R is the gas constant and T is the surface temperature. The kinetic parameters, ν_n , E_{des} and n , uniquely describe the desorption of a particular species from a surface and

can be extracted from experimental TPD spectra using the methods described previously (Bolina et al. 2005a,b; Bolina & Brown 2005). Kinetic parameters obtained for the desorption of pure ices from HOPG are presented in Table 1 (Bolina et al. 2005a,b; Bolina & Brown 2005). To allow a direct comparison with previous data (Sandford & Allamandola 1988, 1993; Fraser et al. 2001), desorption energies are given in temperature units (K). Note that, due to the conversion of the H₂O ice from the amorphous to the crystalline phase during the TPD heating process, the kinetic parameters for H₂O given in Table 1 are for the desorption of crystalline H₂O. To give an indication of the accuracy of these kinetic parameters, Fig. 2 shows a comparison of the experimental data recorded for NH₃ desorption and the simulated TPD spectra for NH₃ that result from inserting the kinetic parameters in Table 1 into the Polanyi–Wigner equation. It can clearly be seen that there is good agreement between the simulated TPD spectra and the experimental data.

Comparing the data in Table 1 with previous results (Sandford & Allamandola 1988, 1993; Fraser et al. 2001) shows reasonable agreement between the desorption energies obtained here and those determined previously. For H₂O we report a desorption energy of 4799 ± 96 K for crystalline H₂O (peak B in Fig. 1), while Fraser et al. (2001) obtained a desorption energy of 5773 ± 60 K and Sandford & Allamandola (1988) reported a binding energy for H₂O on annealed H₂O ice of 5070 ± 50 K. For CH₃OH, our desorption

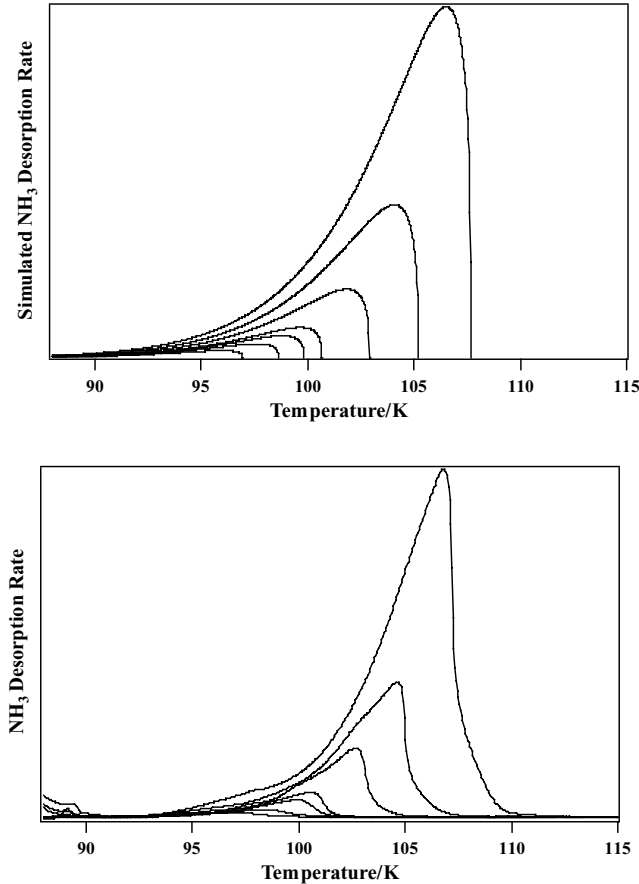


Figure 2. A comparison of experimental TPD spectra (bottom panel) and simulated TPD spectra (top panel) for NH_3 adsorbed on HOPG at 88 K. The simulations were performed using the kinetic parameters given in Table 1.

energy of 4931 ± 98 K is slightly higher than that of 4235 ± 25 K obtained by Sandford & Allamandola (1993). Finally, for NH_3 our desorption energy of 2790 ± 144 K is slightly lower than that of 3075 ± 25 K reported previously (Sandford & Allamandola 1993). It is likely that the small difference in the desorption energies derived in the different experiments is due to the values of desorption order determined for the systems by the three groups, as discussed below.

Whilst the desorption energies obtained in our study and the previous studies are similar, the orders of desorption are rather different. Sandford & Allamandola (1988, 1993) assumed first-order desorption for H_2O , CH_3OH and NH_3 , while Fraser et al. (2001) found that H_2O showed zero-order desorption kinetics. Our results, shown in Table 1, are closer to those of Fraser et al. (2001) and reveal a fractional desorption order. It is useful at this point to discuss the physical significance of the desorption order. H_2O , CH_3OH and NH_3 are all bound weakly to the surface and form physisorbed multilayers of molecular ices. Confirmation of this comes from the low values of desorption energy obtained for these species, here and in previous investigations, which is characteristic of physisorption. A feature of multilayer formation is that the adsorption of one molecule does not affect the adsorption or desorption of other molecules on the surface – that is the rate of desorption is independent of the amount (coverage) of species on the surface. Hence, as shown in equation (1), the species shows zero-order desorption. The previous assumption of Sandford & Allamandola (1988, 1993) that H_2O , CH_3OH and NH_3 obey first-order desorption kinetics is therefore

incorrect. It is also clear from looking at the TPD spectra in Fig. 1 (Bolina et al. 2005a) that H_2O desorption does not show perfect zero-order desorption kinetics. A feature of zero-order desorption is that the TPD spectra share leading edges, which the spectra in Fig. 1 do not. TPD spectra recorded for CH_3OH and NH_3 desorption from HOPG also do not share leading edges and therefore again do not show zero-order desorption (Bolina & Brown 2005; Bolina et al. 2005b). Instead, as seen in Table 1, fractional desorption orders were obtained for H_2O , CH_3OH and NH_3 desorption from the HOPG surface. This fractional desorption order can be attributed to the hydrogen bonding that exists in the molecular ices which ensures that the desorption of one molecule is not independent of the desorption of other molecules. Hydrogen-bonded systems have previously been shown to exhibit fractional-order desorption kinetics (Wu, Truong & Goodman 1993; Nishimura, Gibbons & Tro 1998) and infrared data recorded for H_2O , CH_3OH and NH_3 adsorbed on HOPG (Bolina et al. 2005a,b; Bolina & Brown 2005) also provide evidence for the existence of hydrogen bonding in these pure ice systems. Due to the differences in desorption order between our data and previous data (Sandford & Allamandola 1988, 1993; Fraser et al. 2001), the pre-exponential factors given in Table 1 are also different to those reported previously.

3.2 Desorption under astrophysical conditions

The desorption temperatures for pure H_2O , CH_3OH and NH_3 ices recorded in our experiments (Bolina et al. 2005a,b; Bolina & Brown 2005), and shown for H_2O in Fig. 1, cannot be used directly in astrochemical models. This is because desorption is a non-equilibrium process and hence the temperature at which it occurs is influenced by both the rate of heating of the ice and, for non-first-order processes such as multilayer desorption, by the thickness of the ice. During star formation, the rate at which the temperature rises is dependent on the mass of the star (Viti et al. 2004). Hence, high-mass stars will have a faster heating rate than low-mass stars. It has been shown that a dust grain in a hot core is typically heated at a rate of the order of 1 K century⁻¹ (Viti & Williams 1999; Viti et al. 2004), clearly impractical in laboratory studies.

To determine the extent to which desorption temperatures vary between laboratory and astrophysical conditions we have simulated the desorption of pure H_2O , CH_3OH and NH_3 ices from an HOPG surface at a range of different heating rates. The simulations use a method developed by Collings et al. (2004) and involve calculating the rate of change of gas phase concentration of the desorbing species as a function of temperature. In this way, the simulations produce traces which resemble typical TPD ‘peaks’. Constructing the simulation is a two-step process involving the rate of desorption from the surface and the rate of pumping of the gas phase species out of the system. This can be expressed as

$$\frac{d[\text{ice}_{(g)}]}{dt} = k_d \theta^n - k_p [\text{ice}_{(g)}], \quad (2)$$

where $[\text{ice}_{(g)}]$ is the gas phase concentration of the desorbing molecular ice, θ is the surface coverage, n is the order of the desorption, k_p is the rate of pumping of the gas phase species and k_d is the rate constant for desorption, described in equation (3).

$$k_d = \nu_n \exp\left(\frac{-E_{\text{des}}}{RT}\right). \quad (3)$$

The pumping rate used in each simulated spectrum is scaled in proportion to the heating rate, with a heating rate of 10 K s⁻¹ having a pumping rate of 300 s⁻¹ (the experimentally measured pumping

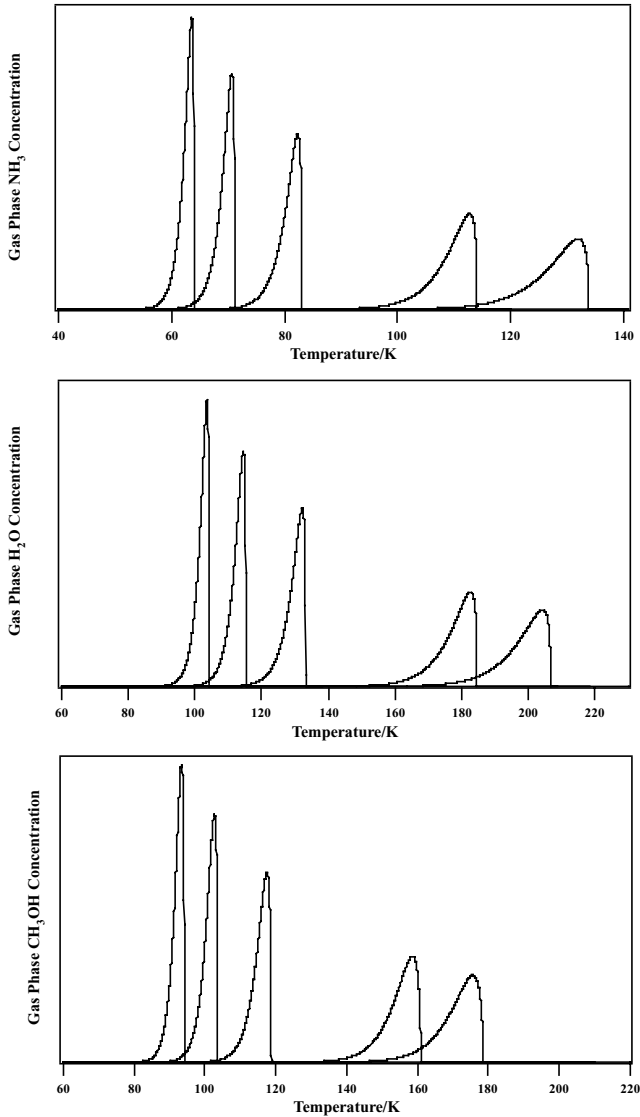


Figure 3. Simulated TPD profiles for NH_3 , H_2O and CH_3OH desorption from HOPG as a function of heating rate. The spectra (from left to right) have a heating rate and pumping speed of 1 K century^{-1} and $9.5 \times 10^{-9} \text{ s}^{-1}$, 1 K yr^{-1} and $9.5 \times 10^{-7} \text{ s}^{-1}$, 1 K day^{-1} and $3.5 \times 10^{-4} \text{ s}^{-1}$, 0.2 K s^{-1} and 6 s^{-1} (0.5 K s^{-1} and 15 s^{-1} for H_2O and CH_3OH multilayers), 10 K s^{-1} and 300 s^{-1} , respectively. The gas phase concentration of each species is given in arbitrary units.

rate). This ensures that the simulations produce peaks on a comparable scale.

Fig. 3 shows the effect of varying the heating rate from 1 K century^{-1} to 10 K s^{-1} on the desorption of NH_3 , H_2O and CH_3OH multilayers from an HOPG surface. The spectra are simulated using the kinetic parameters given in Table 1 and using an initial surface coverage of $9.5 \times 10^{21} \text{ molec m}^{-2}$. This coverage corresponds to a water ice thickness of $0.3 \mu\text{m}$, comparable to the thicknesses of interstellar ices (Collings et al. 2004). In addition to being astrophysically relevant, this ice thickness also allows us to directly compare our data with previous data for H_2O ice calculated by Collings et al. (2004). Fig. 3 clearly shows that, as expected, a change in the heating rate, down to those expected under astrophysical conditions, causes a marked reduction in the desorption temperature of all three molecular species.

The results shown in Fig. 3 can be directly compared to a previous simulation of H_2O desorption from a Au substrate by Collings et al. (2004). Both studies show good agreement in the desorption temperature of H_2O ice at astrophysically relevant heating rates, despite the fact that they were performed on different surfaces. At a heating rate of 1 K century^{-1} , desorption temperatures of 103 and 105 K are evaluated by this study and by Collings et al. (2004), respectively. This suggests that the desorption temperature of H_2O ice at astrophysically relevant heating rates is independent of the substrate used to model the grain surface. This is not surprising since H_2O is physisorbed on both the Au and the HOPG surface, and hence the surface itself does not play a large role in the adsorption. This is important since the exact nature of dust grains in the ISM is still the subject of some debate. It is not possible to compare the results shown in Fig. 3 for CH_3OH and NH_3 desorption with other work as there are no previous simulations of this type for the desorption of pure CH_3OH or pure NH_3 ices under astrophysical conditions.

The simulations presented in Fig. 3 can also be adjusted to more astrophysically relevant environments. In the ISM, there are no pumping effects and so the simulations shown in Fig. 3 have also been run ignoring the effect of pumping. In this case, the gas phase concentration of a species is simply equal to the total number of molecules desorbed from the grain surface. As there is no pumping mechanism in this model, the gas phase concentration of each species saturates when all of the molecules have desorbed from the surface. Fig. 4 shows the gas phase concentration of NH_3 , H_2O and CH_3OH multilayers desorbing from a model grain surface as a function of heating rate and temperature. The simulations use the parameters shown in Table 1 and heating rates from 1 K century^{-1} to 10 K s^{-1} . The simulations were run for an initial surface coverage of $9.5 \times 10^{21} \text{ molec m}^{-2}$, hence the cumulative gas phase desorption saturates at this value. Note that, for each desorption spectrum shown in Fig. 3, the temperature of the desorption peak is identical to the temperature at which desorption to the gas phase is complete for the corresponding heating rate, as seen in Fig. 4.

The data shown in Fig. 4 can be compared with similar simulations, produced using the desorption parameters determined by other groups. Fig. 5(a) shows a comparison of the gas phase concentration of NH_3 as a function of temperature using both our kinetic parameters and those previously determined by Sandford & Allamandola (1993). Both simulations were run using an initial surface coverage of $9.5 \times 10^{21} \text{ molec m}^{-2}$ and a heating rate of 1 K century^{-1} . It is clear from Fig. 5(a) that there is a small difference between the two sets of data, with the simulations based on the kinetic parameters derived by Sandford & Allamandola (1993) showing greater rates of desorption at a given temperature than simulations based on our data. Although the difference in desorption rates is small for a heating rate of 1 K century^{-1} , it will be larger for faster heating rates. Whether or not this small difference will be significant for astrochemical models will depend on the accuracy of the models themselves.

The data shown in Fig. 4 for H_2O desorption can also be directly compared with previous simulations of H_2O desorption performed by Collings et al. (2004). Collings et al. (2004) simulated multilayer water desorption from a Au substrate as a perfect zero-order process. A feature of zero-order desorption is that, for a given heating rate, desorption profiles for varying coverages can be laid on top of each other (Collings et al. 2004). Hence simulations, such as those shown in Fig. 4, can be extrapolated for ice layers of any thickness. However, the simulations presented here for H_2O (and also for NH_3 and CH_3OH) multilayers show fractional, not zero-order desorption. The observation of a fractional desorption order means that it

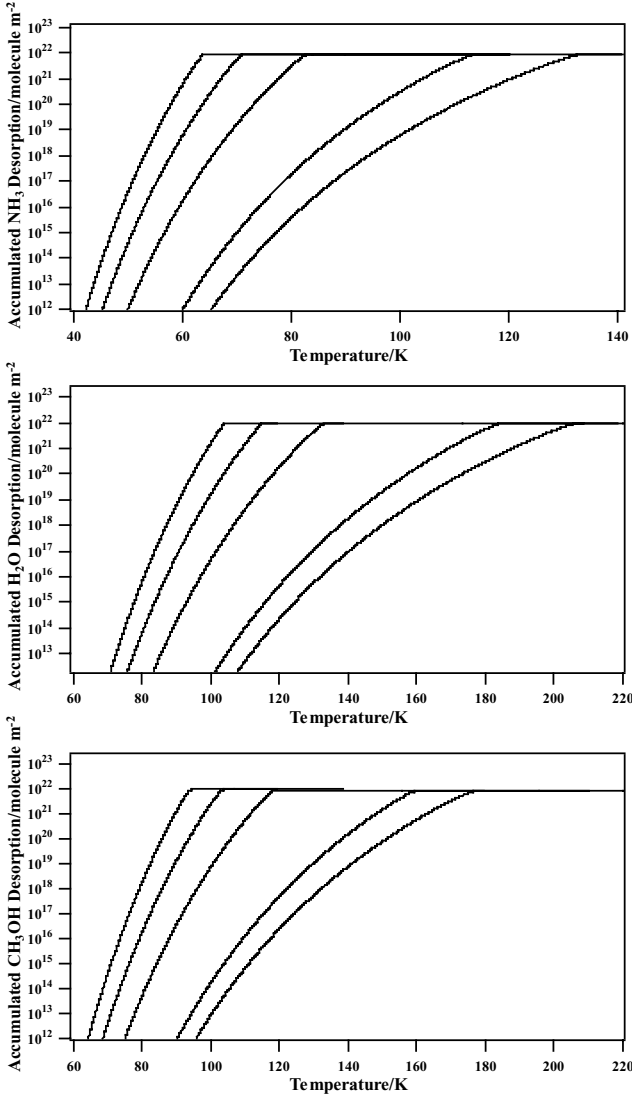


Figure 4. Simulated cumulative desorption to the gas phase for pure NH_3 , H_2O and CH_3OH ices desorbing from HOPG as a function of heating rate. The spectra (from left to right) have a heating rate of 1 K century^{-1} , 1 K yr^{-1} , 1 K day^{-1} , 0.2 K s^{-1} (0.5 K s^{-1} for H_2O and CH_3OH multilayers) and 10 K s^{-1} .

is not possible to overlay desorption traces for different ice thicknesses. An example of this can be seen in Fig. 5(b), which shows the desorption behaviour of varying initial NH_3 ice thicknesses using the kinetic parameters given in Table 1. Whilst the difference between the traces shown in Fig. 5(b) is quite small, it is clear that the curves cannot be laid on top of each other when the desorption order is found to be fractional. Again, whether or not this difference is important in astrochemical models will depend on the accuracy of the models themselves. For faster heating rates than 1 K century^{-1} , the observed difference in desorption rate for different thicknesses of ice will be larger and therefore may be significant, whatever the accuracy of the astrochemical model.

3.3 Gas phase depletion and residence times

An important consequence of gas–grain interactions in the ISM is that molecules are depleted from the gas phase when they are ad-

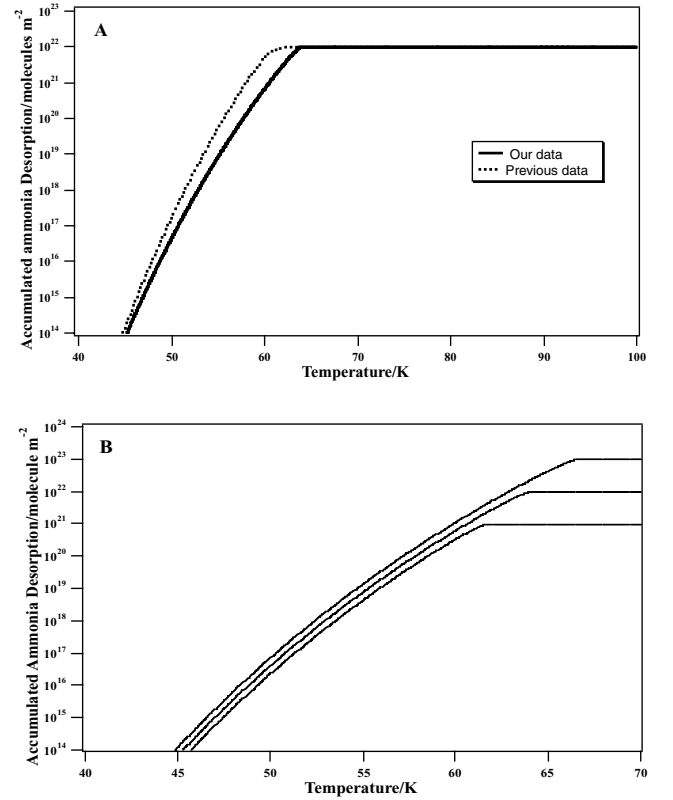


Figure 5. (a) A comparison of the gas phase concentration of NH_3 as a function of temperature using our kinetic parameters and those previously determined by Sandford & Allamandola (1993). Both simulations were run with an initial surface coverage of $9.5 \times 10^{21} \text{ molec m}^{-2}$ and a heating rate of 1 K century^{-1} . (b) The effect on cumulative NH_3 desorption to the gas phase of using different ice film thicknesses for a fractional-order desorption process. The simulated spectra (from top to bottom) represent initial coverages of 9.5×10^{22} , 9.5×10^{21} and $9.5 \times 10^{20} \text{ molec m}^{-2}$ of NH_3 on HOPG. The heating rate is 1 K century^{-1} .

sorbed on the surface of dust grains. The rate of depletion from the gas phase is an important consideration in modelling the true column density of molecules present in dark clouds such as H_2O , CH_3OH and NH_3 (Sandford & Allamandola 1993). The residence time of a molecule on a dust grain, and hence the rate of depletion, can be calculated as a function of grain temperature using the kinetic parameters shown in Table 1. The residence time is equal to $1/k_d$, where k_d is defined as in equation (3). In order to compare the simulations presented here with previous studies, which have differing orders of desorption, residence times are presented as the half-life of the surface population. The half-life $t_{1/2}$ is defined as the time taken for the surface population to fall to half of its original value and can be calculated using equation (4):

$$t_{1/2} = \frac{\left(\frac{1}{1-n}\theta_0^{1-n}\right)(1 - 0.5^{1-n})}{k_d}, \quad (4)$$

where n is the order of the desorption process, θ_0 is the initial surface coverage and k_d is defined in equation (3). As clearly shown in equation (4), for all cases except pure first-order desorption, the half-life depends on the initial surface coverage of the molecular ice. In the calculations presented here, the initial surface coverage was fixed at $1.15 \times 10^{21} \text{ molec m}^{-2}$, in agreement with previous studies (Fraser et al. 2001). This concentration is equivalent to ~ 100

Table 2. Table showing the half-life of H₂O molecules on an HOPG model grain surface as a function of temperature. The data from this study are shown in bold. Also included, for comparison, are data previously calculated by Fraser et al. (2001) and Sandford & Allamandola (1988).

| Temperature (K) | Half-life ($t_{1/2}$ yr) | | |
|-----------------|---|-----------------------|-------------------------------|
| | This study | Fraser et al. (2001) | Sandford & Allamandola (1988) |
| 10 | 2.6×10^{189} | 8.8×10^{231} | 6.8×10^{200} |
| 20 | 1.6×10^{85} | 8.6×10^{105} | 5.5×10^{90} |
| 30 | 2.9×10^{50} | 8.5×10^{63} | 1.1×10^{54} |
| 40 | 1.2×10^{33} | 8.4×10^{42} | 4.9×10^{35} |
| 50 | 4.7×10^{22} | 2.1×10^{30} | 4.8×10^{24} |
| 60 | 5.3×10^{15} | 8.4×10^{21} | 2.2×10^{17} |
| 70 | 5.7×10^{10} | 8.4×10^{15} | 1.3×10^{12} |
| 80 | 1.1×10^7 | 2.7×10^{11} | 1.5×10^8 |
| 90 | 1.4×10^4 | 8.4×10^7 | 1.3×10^5 |
| 100 | 6.7×10^1 | 1.3×10^5 | 4.6×10^2 |
| 110 | 8.5×10^{-1} | 6.8×10^2 | 4.6×10^0 |
| 120 | 2.3×10^{-2} | 8.4×10^0 | 9.8×10^{-2} |
| 130 | 1.0×10^{-3} | 2.0×10^{-1} | 3.8×10^{-3} |
| 140 | 7.4×10^{-5} | 8.4×10^{-3} | 2.3×10^{-4} |
| 150 | 7.6×10^{-6} | 5.3×10^{-4} | 2.1×10^{-5} |

layers of ice, which is the number of molecules expected to accrete on a dust grain during the lifetime of a dark cloud (Hasegawa & Herbst 1993).

The half-life of H₂O molecules within H₂O multilayers, as a function of temperature, is shown in Table 2. Table 2 also lists the half-life of H₂O molecules on H₂O ice surfaces determined using the kinetic parameters evaluated by Fraser et al. (2001) and Sandford & Allamandola (1988). In both of the previous studies, H₂O desorption from the multilayer (or the desorption of H₂O from H₂O ice) was modelled for the desorption of crystalline and amorphous ice. The simulations presented here relate only to the desorption of crystalline ice, as already noted, as the kinetic parameters in Table 1 were evaluated for crystalline H₂O ice only (Bolina et al. 2005a).

Table 2 shows that there is a difference in the half-life of H₂O molecules on H₂O ice surfaces across the three studies. This study shows that H₂O would remain on the surface for an appreciable time (defined as a time longer than 10² yr) up to a temperature of 90–100 K, while Fraser et al. (2001) noted a temperature of 110–120 K and Sandford & Allamandola (1993) noted a temperature of 100–110 K. This difference can be explained by the different kinetic parameters used in the different simulations, in particular the order of desorption and pre-exponential factors. This study modelled desorption as a fractional-order process, while the study by Fraser et al. (2001) modelled H₂O desorption as a zero-order process and Sandford & Allamandola (1993) modelled the desorption as a first-order process.

Similar analysis has been carried out to calculate the half-life of multilayers of NH₃ adsorbed on the surface of model dust grains. Table 3 lists the half-life of NH₃ calculated in this study and in a previous study by Sandford & Allamandola (1993). Table 3 shows that there is generally good agreement between this study and the previous work, with both studies showing that NH₃ can remain on the surface of dust grains up to a temperature of ~60 K. This agreement is encouraging, although rather surprising, since the two studies employ completely different kinetic parameters.

Table 4 shows a similar analysis carried out to determine the half-life of CH₃OH molecules on CH₃OH ice. In contrast to the NH₃, there is a small difference between the calculated half-life of CH₃OH

Table 3. Table showing the half-life of NH₃ molecules on an HOPG model grain surface as a function of temperature. The data from this study are shown in bold. The table also shows previous results obtained by Sandford & Allamandola (1993).

| Temperature (K) | Half-life ($t_{1/2}$ yr) | |
|-----------------|---|-------------------------------|
| | This study | Sandford & Allamandola (1993) |
| 10 | 1.9×10^{103} | 2.2×10^{113} |
| 15 | 7.5×10^{62} | 6.8×10^{68} |
| 20 | 4.7×10^{42} | 3.8×10^{46} |
| 25 | 3.6×10^{30} | 1.7×10^{33} |
| 30 | 3.0×10^{22} | 2.1×10^{24} |
| 35 | 5.1×10^{16} | 9.1×10^{17} |
| 40 | 2.4×10^{12} | 1.6×10^{13} |
| 45 | 1.0×10^9 | 3.0×10^9 |
| 50 | 2.1×10^6 | 3.3×10^6 |
| 55 | 1.3×10^4 | 1.2×10^4 |
| 60 | 1.9×10^2 | 1.2×10^2 |
| 65 | 5.3×10^0 | 2.2×10^0 |
| 70 | 2.5×10^{-1} | 7.6×10^{-2} |
| 75 | 1.7×10^{-2} | 4.1×10^{-3} |
| 80 | 1.7×10^{-3} | 3.1×10^{-4} |
| 85 | 2.2×10^{-4} | 3.3×10^{-5} |
| 90 | 3.5×10^{-5} | 4.4×10^{-6} |

in this study and that obtained by Sandford & Allamandola (1993). This study shows that CH₃OH can remain on the surface of dust grains at temperatures up to ~90 K, while Sandford & Allamandola (1993) calculated a temperature of ~80 K. This discrepancy most probably arises from the differences in the kinetic parameters used in the two calculations, and shows the importance of using correct desorption orders to determine kinetic parameters for CH₃OH desorption.

4 ASTROPHYSICAL IMPLICATIONS

The new results reported here need to be taken into account in astronomical situations in which ice-coated dust grains are warmed from

Table 4. Table showing the half-life of CH_3OH molecules on an HOPG model grain surface as a function of temperature. The data from this study are shown in bold. For comparison, the table also shows previous results obtained by Sandford & Allamandola (1993).

| Temperature (K) | Half-life ($t_{1/2}$ yr) | |
|-----------------|---|-------------------------------|
| | This study | Sandford & Allamandola (1993) |
| 10 | 4.2×10^{178} | 8.4×10^{163} |
| 20 | 2.3×10^{79} | 9.2×10^{71} |
| 30 | 1.9×10^{46} | 2.0×10^{41} |
| 40 | 5.6×10^{29} | 9.6×10^{25} |
| 50 | 6.6×10^{19} | 6.1×10^{16} |
| 60 | 1.6×10^{13} | 4.5×10^{10} |
| 70 | 3.0×10^8 | 1.9×10^6 |
| 80 | 8.6×10^4 | 9.8×10^2 |
| 90 | 1.5×10^2 | 2.7×10^0 |
| 100 | 9.3×10^{-1} | 2.5×10^{-2} |
| 110 | 1.5×10^{-2} | 5.2×10^{-4} |
| 120 | 4.6×10^{-4} | 2.1×10^{-5} |
| 130 | 2.4×10^{-5} | 1.4×10^{-6} |
| 140 | 2.0×10^{-6} | 1.4×10^{-7} |
| 150 | 2.3×10^{-7} | 1.8×10^{-8} |

their normally low temperatures (typically ~ 10 – 20 K) to temperatures of the order of 100 K. Such warming is well known to occur in material near to young massive stars, in so-called hot cores, over time-scales of 10^4 – 10^5 yr (Viti et al. 2004). It is now well established that similar warming also occurs, to somewhat lower temperatures, in material near to young stars of relatively low mass, although perhaps over a longer time-scale (Bottinelli et al. 2004).

In addition to occurring in star-forming regions, the loss of icy mantles is also believed to occur in dynamical events in the ISM, such as the passage of shocks and in turbulent interfaces between gas flows. The passage of stellar jets from young outward flows through the natal cloud creates such an interface within which a characteristic chemistry arises from the interaction (Viti, Natarajan & Williams 2002). Where those stellar jets' impact on distant molecular clouds the resultant dynamical and radiative interaction (in a so-called Herbig–Haro object) also removes mantles and leads to photoreactions that create a signature chemistry that has been frequently observed (Girart et al. 2005).

The desorption data provided here are for pure H_2O , pure NH_3 and pure CH_3OH ices adsorbed on grain surfaces. Real interstellar ices are not composed of pure molecular species and instead consist of a broad range of molecules, including those discussed here. The extent to which interstellar ices are found in chemically distinct layers is currently unclear. However, ices that are apparently layered, and also mixed, can both be observed in the ISM (Gibb et al. 2004). Hence, studying pure ice systems does give insight into the sublimation behaviour of segregated interstellar ices.

The new data reported here confirm that pure ices begin to desorb once the dust temperature rises significantly above its normal low value. Evaporation for pure H_2O ice is rapid ($\sim 10^4$ yr) for temperatures ~ 90 K. For pure CH_3OH ice, evaporation is rapid at ~ 85 K and for pure NH_3 ice sublimation occurs at ~ 55 K. Thus, as warming occurs, the chemical composition of the layered ices and of the gas phase will vary in a predictable way which can be incorporated into appropriate astrochemical models. It is only with the incorporation of this new data into astrochemical models that it will become clear whether or not the data presented here are significant for star-forming regions. Preliminary studies of the effect that the new data

for H_2O have on astrochemical models (Brown et al. 2006) suggest that differences are observed for low-mass stars. However, further work is necessary to determine the effects of this data under a range of different conditions.

5 CONCLUSIONS

This paper reports the results of new experiments on the desorption of pure molecular ices from a model grain surface. The experimental data have been used to determine the desorption temperatures of these ices under interstellar conditions, and the results obtained for the desorption of H_2O ice are in good agreement with previous results (Collings et al. 2004). The half-lives of these ices against thermal desorption are also presented as a function of temperature. For H_2O ice, there is some variation between the half-lives calculated here and those determined previously (Sandford & Allamandola 1993; Fraser et al. 2001); however, for NH_3 ices the agreement between our data and previous studies (Sandford & Allamandola 1993) is good. For the sublimation of pure CH_3OH ices, there is only a small difference between our data and previous data (Sandford & Allamandola 1993). These results show the importance of laboratory data for the understanding of astronomical situations in which dust grains coated with icy mantles are warmed by nearby stars or dynamical events.

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